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We hypothesize that during pyrolysis of lignites, the primary evolution of gas occurs from lignin-related residues in the coal. Likely pathways for this primary gas release have been theoretically modelled by a set of thermally-allowed pericyclic reactions that respectively lead to each of methane, carbon monoxide, carbon dioxide, and water products from substrates containing lignoid moieties. The model pathways for methane formation can be experimentally examined by pyrolysis of a series of methoxy-benzenes, e.g.,

anisole MeO-c1ccccc1, guaiacol MeO-c1ccccc1O, and iso-eugenol MeO-c1ccc(cc1)/C=C/O.

Experiments over the temperature range 200-500 C in batch tubing-bomb reactors equipped for gas and liquid product analyses showed that guaiacol was appreciably more reactive than anisole, fractional conversions of these substrates at 420 C and 120 s being respectively 0.083 and 0.0022. The former pyrolysis was essentially first order both in guaiacol disappearance as well as in methane gas appearance and yielded Arrhenius parameters ( $\log_{10} A \text{ s}^{-1}$ ,  $E^* \text{ kcal/mol}$ ) = (11.5, 45.8). These data accord with the hypothesis that methane release from guaiacyl moieties occurs by a concerted molecular group-transfer reaction.